PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B01D 53/28

A2

(11) International Publication Number: WO 00/35562

(43) International Publication Date: 22 June 2000 (22.06.00)

(21) International Application Number: PCT/US99/30064

(22) International Filing Date: 16 December 1999 (16.12.99)

(30) Priority Data:

60/112,546	16 December 1998 (16.12.98)	US
09/291,339	14 April 1999 (14.04.99)	US

(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(72) Inventors: THOMAS, Raymond, Hilton, Percival; 5990 Hopi Court, Pendleton, NY 14094 (US). ROBINSON, Roy, Philip; 38 Andrews Avenue, Cheektowaga, NY 14225 (US). WILLIAMS, David, John; 6202 Shamrock Lane, East Amherst, NY 14051 (US). LOGSDON, Peter, Brian; 38 East Royal Hill Drive, Orchard Park, NY 14127 (US).

(74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc., Law Dept., Attn: A. Olinger, 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

Without international search report and to be republished upon receipt of that report.

(54) Title: PROCESS FOR SEPARATING WATER FROM CHEMICAL MIXTURES

(57) Abstract

The present invention relates to novel compositions of drying agents of superabsorbent polymers, molecular sieves and mixtures thereof and binders of polyurethane foam, polyisocyanurate foam and supports comprising cellulose and a method for separating, drying and/or filtering chemical mixtures. The composition and method of the invention have broad applicability. They may be used for example to remove water from chemical mixtures like refrigerants (e.g., in vehicular refrigeration systems), air (e.g., in vehicular braking systems), natural gas and cleaning solvents (e.g., used in semiconductor manufacture and pipeline cleaning).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PROCESS FOR SEPARATING WATER FROM CHEMICAL MIXTURES

Cross Reference to Related Applications

This application is a continuation-in-part of pending U.S. Patent Application Serial No. 08/967,632 filed November 10, 1997. Priority is claimed from pending Provisional Patent Application Serial No. 60/112,546 filed December 16, 1998. Both of these applications are incorporated herein by this reference.

Field of the Invention

The present invention relates to novel desiccant compositions comprised of certain drying agents and binders and a method for separating, drying and/or filtering chemical mixtures. The composition and method of the invention have broad applicability. They may be used for example to remove water from chemical mixtures like refrigerants (e.g., in vehicular air conditioning systems), air (e.g, in vehicular braking systems), natural gas and cleaning solvents (e.g., in semiconductor manufacture and pipeline cleaning).

Background of the Invention

A number of methods have been developed in order to separate water from chemical mixtures. The known methods include the use of alkaline earth compounds, carbon molecular sieves, oleum, distillation, and membranes. Many of the known methods are disadvantageous because the processes are inefficient or uneconomical; the drying agents undergo undesirable side reactions and/or adsorbs or absorbs the material being dried (See, U.S.P. 5,347,822).

Drying agents used principally in connection with circulating refrigerants include activated aluminum oxide, silica gels and molecular sieves in solid or granulated form. During use, these materials are abraded by the flow of the cooling liquid and mechanical vibrations and form dust particles. In order to prevent the dust from clogging the valves and conduits of the refrigeration system, a filter must be employed. This costs time (for installation) and money.

The compositions and method of the invention overcome the difficulties associated with the prior art. In particular, we have found that certain of the compositions eliminate the need for a separate filter element.

Summary of the Invention

A composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

A process comprising contacting a chemical mixture comprising water with an effective amount of a composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose

Detailed Description of the Invention

A. The Desiccant Composition

The invention relates to a desiccant composition comprising a drying agent and a binder. Specifically, the invention relates to the following compositions: A composition comprising a drying agent and a binder wherein: (a) said drying agent

comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

In another embodiment, the drying agent comprises an effective amount of a molecular sieve and said binder comprises from 30 to 75 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

In yet another embodiment, the drying agent comprises 50 weight percent of a molecular sieve and said binder comprises from 50 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

1. Drying Agent

For purposes of this invention the following terms have the indicated meanings: "Polymer" means a homopolymer, copolymer (not limited to only two components), or mixtures thereof having a molecular weight of from 1,000,000 to 100,000,000 and preferably from 10,000,000 to 100,000,000 and more preferably from 85,000,000 to 100,000,00 and which are crosslinked sufficiently to impart moisture absorbing or adsorbing properties; "Superabsorbent Polymer" means a Synthetic or Semi-Synthetic (defined below) Polymer that swells, to at least twice its dry volume, with the addition of water at room temperature after standing for up to two hours; Semi-Synthetic means a derivative of a naturally occurring Polymer; and "Synthetic" means a Polymer produced through chemical reaction.

Exemplary Semi-Synthetic Polymers include, without limitation, cellulose ethers, modified starches, starch derivatives, natural gum derivatives, and mixtures thereof. Illustrative Synthetic Polymers include, without limitation, polymers, related polymers, and polymer salts of acrylamide, acrylic acid, ethylene oxide, methacrylic

acid, polyethyleneimine, polyvinyl alcohol, polyvinyl pyrrolidone, and mixtures thereof. For purposes of this invention "related polymer" means that the polymer repeat unit, or a branch thereof, is extended by carbon atoms, preferably from one to four carbon atoms. For example, a related polymer of acrylic acid is one in which the vinyl group is extended by one carbon to form an allyl group.

Synthetic Polymers are preferred. Polyacrylic acid and its salts are more preferred and sodium polyacrylate (such as SXM70 and SXM77 from Stockhausen of Greensboro, North Carolina) and potassium polyacrylate are most preferred.

Any molecular sieve may be used in the composition of the invention. These materials are commercially available from for example UOP of Des Plaines, Illinois and Grace Corporation of Baltimore, Maryland. They may also be prepared by methods well known in the art. Suitable molecular sieves include without limitation: Type A, Type B, Type L, Type X, Type Y and mixtures thereof. In the practice of this invention Type A is preferred. For refrigeration applications molecular sieves of 3 – 4 Angstroms are preferred such as XH6, XH7, XH9 and XH11 from UOP.

Multiple drying agents may be used in the compositions and method of the invention. Besides Superabsorbent Polymers and molecular sieves, other known drying agents can optionally be employed in the compositions of the invention. They include without limitation activated alumina, activated carbon, silica gel and mixtures thereof. When multiple drying agents are used they may be used in any ratio that is from 1 to 99 to 99 to 1.

The selection of drying agent(s) including type and form will depend on the process (including materials and equipment) that produces the chemical mixture or in which the chemical mixture is being used. The shape and hardness of the drying agent should be chosen to withstand the rigors of the system in which it is used and to avoid entrainment in the equipment, plugging openings and conduits. The drying agent may be a powder, fine particles, fibers, or a shaped piece or pieces. We have found that a 50/50 mixture of superabsorbent polymer and molecular sieve (with 50 weight percent binder) provides superior capacity and drying ability than either drying agent

alone in a process for separating water from halogenated hydrocarbons, for example a refrigerant such as R-134a.

2. Binder

Any material capable of supporting the drying agent (including water absorbed/adsorbed in the drying agent) when may be used in the invention. Suitable binder materials include, without limitation, organic plastic binders such as isocyanate-based polymers, phenolic resins, aliphatic epoxy resins, silicone, polyvinyl alcohol resins, polyphenylene sulfide, poly(ether ketone), polyether sulfone, supports comprising cellulose and mixtures thereof. Polyurethane foam, polyisocyanurate foam and supports comprising cellulose are preferred. These materials are known in the art and can be purchased commercially or prepared by known methods. See, for example, U.S.P.'s 4,986,930, 4,655,757, 4,340,556, 4,596,567, 2,882,244, 2,950,952, 2,882,243 and 3,130,007 the disclosures of which are hereby incorporated by reference.

It is important to select a binder material that can be processed at a temperature that does not destroy the drying agent. In the case of thermoplastic binders, the processing temperature should be less than 300°C, preferably less than 250°C.

The desiccant compositions of the invention can be prepared by adding the drying agent as one of the components in the process (e.g, polymerization) used to prepare the binder. When a polyurethane foam or polyisocyanurate foam binder is used, the desiccant composition can be prepared by adding the drying agent with the other foam ingredients from the same or a different mix head and foaming the mixture. If a preblend of the foam ingredients is used, the drying agent can be added to the "A" and/or "B side" of the preblend. Preferably it is added to the "B side".

When cellulose is the binder, preferably, the desiccant composition has a laminate structure (i.e, layered e.g., binder/drying agent/binder etc.) Desiccant compositions which utilize a support comprising cellulose may be prepared by following the procedure outlined in European Patent Application 0 359 615.

The amount of drying agent and binder utilized in the desiccant composition is application dependent. Each should be used in "effective amounts" where this term means that amount of drying agent and optionally binder necessary to achieve a desired degree of dryness, separation and/or filtering and that amount of binder necessary to support the drying agent. This amount is readily determined by consideration of the amount of water sought to be separated, the flow rate of the chemical mixture, and the adsorptive or absorptive characteristics of the drying agent and binder. Generally, the desiccant compositions have the compositions disclosed in Table I below. The numerical ranges are understood to be prefaced by "about."

Table I

Desiccant Composition	Range (wt.%)	Preferred Range (wt.%)	More Preferred Range (wt.%)	Most Preferred Range (wt.%)
Drying agent	10 – 80	20 – 75	30 – 70	40 – 65
Binder	90 – 20	80 – 25	70 – 30	60 – 35

The requisite initial dryness of the drying agent will depend on such factors as the amount of water in the chemical mixture to be dried, the amount of drying agent used, and the equilibrium concentration of water in the drying agent when it is in contact with the chemical mixture at its final, or desired, water content. Preferably, the drying agent is dried to the greatest extent possible prior to. The temperature at which the drying agent is dried should be high enough to remove water without degrading the drying agent. In the case of molecular sieves this drying is conducted generally in a vacuum desiccator at temperatures up to 300°C. In the case of Superabsorbent Polymers the drying is conducted again in a vacuum desiccator but at temperatures between 100 and 200°C. As the drying agent loses water, its weight decreases until it reaches a constant weight. At this point, the drying agent has been dried to the greatest extent possible at that particular temperature.

If the application requires that all but 10 ppm or less of water be removed from the chemical mixture, it may be necessary to use an essentially anhydrous Water-Soluble Polymer. For purposes of this invention, "essentially anhydrous" means that the drying agent contains less than 1 weight percent water.

B. Process

The amount of desiccant composition utilized will depend again on the application. An effective amount of the desiccant composition should be used where this term means an amount necessary to achieve a desired degree of dryness, separation and/or filtering. This amount is readily determined by consideration of the amount of water sought to be separated, the flow rate of the chemical mixture, and the adsorptive or absorptive characteristics of the drying agent and binder. Generally, the desiccant composition is used in an amount of from 3 to 700 percent, preferably from 100 to 700 percent and most preferably from 200 to 700 percent based upon the amount of water to be removed.

In another embodiment, the invention relates to a process comprising: contacting a chemical mixture comprising water with a drying effective amount of a desiccant composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

For purposes of this invention, a chemical mixture is a liquid, gaseous or partially gaseous mixture of water and at least one inorganic material, organic material, or mixtures thereof. Illustrative inorganic materials include, without limitation, air, hydrogen, hydrogen chloride, sulfur dioxide, sulfur trioxide, carbon

monoxide, carbon dioxide, boron trifluoride, uranium hexafluoride, sulfur hexafluoride, arsenic pentafluoride, halide salts, nitric acid, sulfuric acid, chlorine, metal ions, non-aqueous inorganic solvents, and mixtures thereof. Exemplary organic materials include, without limitation, alcohols such as methanol, ethanol and propanol, ketones including acetone, and aromatics including benzene, toluene and naphthalene, hydrocarbons, including gaseous hydrocarbons such as methane, ethane, propane and butane; and halogenated hydrocarbons such as chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons, chlorocarbons, hydrochlorocarbons, hydrofluoroethers, fluoroethers, and mixtures thereof, including without limitation difluoromethane, trifluoroethane, tetrafluoroethane, pentafluoroethane, pentafluoropropane and the like.

The process of the invention may be carried out in any suitable vessel. In the process of the invention, the chemical mixture is contacted with the desiccant composition for from 1 to 24 hours, preferably from 1 to 6 hours and most preferably from 1 to 4 hours.

In a particular application of the process embodiment, the desiccant composition is utilized in a refrigeration system such as a car air conditioning system to absorb water from the refrigerant. In this application, the process comprises cycling a refrigerant in a system wherein the refrigerant is condensed and thereafter evaporated, said system comprising an effective amount of a composition comprising an drying agent and a binder wherein said drying agent comprises an effective amount of a material selected from the group consisting of superabsorbent polymer, molecular sieve and mixtures thereof and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam and a support comprising cellulose.

In this application, the desiccant composition may comprise the core of a drier. A drier core which utilizes a drying agent of the invention with a polyurethane foam or polyisocyanurate foam binder, may be prepared by adding the drying agent to a foam formulation in the manner discussed above and foaming the composition in a container, the resulting desiccant composition would comprise the core and the

container the drier. A drier core which utilizes a drying agent of the invention and a support comprising cellulose as the binder, can be prepared by adding the drying agent to the cellulose binder as discussed above and rolling or stacking the resulting composition in a container. The desiccant composition would once again comprise the core and the container the drier. This drier core would be fixed in the refrigeration system in the circulation path by means known in the art.

Applicants have discovered that a desiccant compositions comprising a mixture of a Superabsorbent Polymer and molecular sieve and a polyurethane or polyisocyanurate foam binder are particularly useful in this process embodiment especially at loadings of 50 weight percent drying agent (50:50 ratio of drying agents) and 50 weight percent foam. This composition exhibits several advantages over prior art materials including greater capacity and drying ability, smaller volume and elimination of a separate filter element.

In another application of the process of the invention, the invention can be used to absorb water from spent cleaning solvent such as that used in semiconductor manufacture or natural gas or other pipeline cleaning. The process would comprise exposing a solvent comprising water to a desiccant composition of the invention. This could be done after the solvent was recovered as a separate step or during the cleaning process itself. In the latter application, the desiccant composition would be fixed, for example, to the inside of a pipeline and the solvent in the course of passing through the pipeline would pass through the desiccant and water would be removed from the solvent. In still another application of the process of the invention, the invention can be used to absorb water from air such as for example in air brake applications.

In all embodiments, the performance of the drying agent may be improved by periodically regenerating the drying agent to release the water separated from the chemical mixture. Regeneration may be accomplished by any convenient means, such as by heating the drying agent to a temperature suitable to release water from the drying agent.

The amount of water removed by the Superabsorbent Polymer must be monitored in order to maintain its mechanical integrity. If the Superabsorbent Polymer is in solid form, allowing the amount of water separated from the chemical mixture by the Superabsorbent Polymer to reach a level at which it turns from a solid into a gel or liquid may be disadvantageous. The amount of water at which this phase change occurs will vary depending on the Superabsorbent Polymer used but is readily determined by routine experimentation. Preferably, the Superabsorbent Polymer is used to a point just below the point at which a phase change occurs. Water separation may be monitored by any convenient means as for example, measuring the amount of water in the chemical mixtures. Further, if one or more other chemicals in the chemical mixture forms a gel or solid with the Superabsorbent Polymer, the water required for the solid to liquid phase change may be altered.

If very low levels of water are desired in the chemical mixture, that mixture may be treated sequentially with more than one drying agent bed to reach the desired level. We have discovered the use of a sodium polyacrylate polymer bed followed by a molecular sieve bed is particularly effective. Alternatively, the process of the invention may be used in conjunction with other well known drying methods.

The invention will be clarified further by a consideration of the following examples, which are purely exemplary.

Examples

Example 1

This example demonstrates the preparation of a desiccant composition comprising polyurethane foam and a superabsorbent polymer. The isocyanate or A component of the mixture used was Mondur 2OS available from Bayer Corporation. The formulation of the B component of the mixture was as follows:

50 parts VORANOL-490 (polyol available from Dow Chemical Co.)

50 parts VORANOL-391 (polyol available from Dow Chemical Co.)

2.5 parts L-6164 (surfactant available from Goldschmidt Chemical Co.)

3.2 parts POLYCAT 41 (catalyst available from Air Products and Chemicals)

53 parts HCFC-141b (blowing agent available from AlliedSignal Inc.).

The A and B side were mixed together and sodium polyacrylate (constituting 43 weight percent of the entire mixture) was added to the mixture and quickly stirred. The whole mass was then poured into a 150 cc Teflon vessel. The vessel was capped and the foam allowed to rise. The vessel was equipped with ports on both ends so that gaseous refrigerant could be passed through it.

Example 2

A sample of R-134a containing 578 ppm water was passed through the vessel described in Example 1 above which contained 27 grams of the potassium salt of polyacrylic acid and foam (The potassium salt of polyacrylic acid comprised 43% of the composition). The moisture content on exiting the vessel was measured using a Karl Fischer coulometer and found to be 25 ppm.

Example 3

The experiment of Example 2 is repeated except that R-134a containing 1114 ppm water was passed through a different vessel containing 51.3 grams of the desiccant composition (containing 43% of the potassium salt of polyacrylic acid). The moisture content on exiting the vessel was 23 ppm.

Example 4

A desiccant composition was prepared as in Example 1 except that the sodium polyacrylate constituted 70 weight percent of a 30 gram sample. Wet nitrogen was passed through the vessel until the desiccant composition had absorbed 20% of its dry weight in water. R-134a was then passed through the vessel very slowly. The exiting R-134a had a moisture content of 180 ppm. This example demonstrates the superior capacity of the desiccant composition in that even after having absorbed 20% of its

dry weight in water, the moisture concentration is far below that reported in the 1994 ASHRAE Handbook for molecular sieve (800 ppm at 16% of its dry weight in water). (I do not understand this)

Example 5

A desiccant composition is prepared as in Example 1 except that the polyol used is polybutylene oxide and the sodium polyacrylate constitutes 60 weight percent of a 30 gram sample. Wet nitrogen is passed through the vessel until the desiccant composition absorbs 20% of its dry weight in water. R-134a is passed through the vessel very slowly. The exiting R-134a has a moisture content of 180 ppm.

Example 6

A desiccant composition is prepared as in Example 1 except that the polyol used is polypropylene oxide and the sodium polyacrylate is 60 weight percent of a 30 gram sample. R-134a is passed through the vessel very slowly. The exiting R-134a has a moisture content of 180 ppm.

Example 7

Sodium polyacrylate deposited on cellulosic material was obtained from Gelok International. The material's tradename is 9525 s/s. A strip that measured 16 in. x 2 in. was rolled to fit into a stainless steel cylinder that was 11.5 in. tall with a diameter of 1.5 in. The cylinder was initially open at both ends. Two ends with tube connection were then bolted on to the cylinder. This fixture was then connected to an apparatus comprising a pump, a supply cylinder of dry R-134a, a flow meter and a loop that bypassed the fixture. The loop contained Celite that was saturated with water. A Panometrics MIS2 probe for measuring the moisture in liquid refrigerants was attached in line with the fixture. The apparatus, with the refrigerant supply cylinder valves closed, was evacuated. The valves were then opened and liquid refrigerant fed to the pump and the pump turned on. In order to wet the refrigerant, the fixture was closed off and the refrigerant fed through the bypass loop. The bypass was then closed and the fixture opened. The reading on the probe was initially off

scale indicating a very high moisture level. After a few minutes the probe registered 380 ppm. After three hours the concentration of water in the R-134a was measured to be 100 ppm.

Example 8

A rigid, open-celled foam was blown into a cylinder that was 4 in. long and 1.5 in. in diameter. The foam formulation contained a mixture of sodium polyacrylate and molecular sieve (7.25 grams each). The cylinder was initially open at both ends. Two ends with tube connection were then bolted on to the cylinder. This fixture was then connected to an apparatus comprising a pump, a supply cylinder of dry R-134a, a flow meter and a loop that bypassed the fixture. The loop contained Celite that was saturated with water. A Panometrics MIS2 probe for measuring the moisture in liquid refrigerants was attached in line with the fixture. The apparatus, with the refrigerant supply cylinder valves closed, was evacuated. The valves were then opened and liquid refrigerant fed to the pump and the pump turned on. In order to wet the refrigerant, the fixture was closed off and the refrigerant fed through the bypass loop. The bypass was then closed and the fixture opened. The reading on the probe was initially off scale indicating a very high moisture level. After 6 minutes the probe registered 528 ppm. After 50 minutes the concentration of water in the R-134a was measured to be 86 ppm.

What is claimed is:

1. A composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

2. The composition of claim 1 (a).

3. The composition of claim 1 (b).

4. The composition of claim 1 (c).

5. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 10 to 80 weight percent and said binder is present in an amount of from 20 to 90 weight percent.

6. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 20 to 75 weight percent and said binder is present in an amount of from 25 to 80 weight percent.

7. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 30 to 70 weight percent and said binder is present in an amount of from 30 to 70 weight percent.

8. The composition of claim 2 or 4 wherein said drying agent is present in an amount of from 40 to 65 weight percent and said binder is present in an amount of from 35 to 60 weight percent.

9. The composition of claim 1 (b) wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises from 30 to 75 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

10. The composition of claim 1 (b) wherein said drying agent comprises 50 weight percent of a molecular sieve and said binder comprises 50 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

11. The composition of claim 1 (a) wherein said support has a laminate structure.

12. The composition of claim 1 (b) wherein said binder is polyurethane foam.

13. The composition of claim 1 (b) wherein said binder is polyisocyanurate foam.

14. The composition of claim 1 (c) wherein said superabsorbent polymer comprises sodium polyacrylate or potassium polyacrylate.

15. The composition of claim 1 (c) wherein said binder comprises polyurethane foam.

16. The composition of claim 1 (c) wherein said binder comprises polyisocyanurate foam.

17. The composition of claim 1 (c) wherein said binder comprises a support comprising cellulose.

18. The composition of claim 17 wherein said support has a laminate structure.

19. A process comprising contacting a chemical mixture comprising water with an effective amount of a composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying

agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

20. A process comprising contacting a chemical mixture comprising water and a halogenated hydrocarbon with an effective amount of a composition comprising a drying agent and a binder wherein: (a) said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose; (b) said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam; or (c) said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

21. The process of claim 20 wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises an effective amount of a support comprising cellulose.

22. The process of claim 20 wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises at least 25 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

23. The process of claim 20 wherein said drying agent comprises an effective amount of a superabsorbent polymer and molecular sieve and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

24. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 10 to 80 weight percent and said binder is present in an amount of from 20 to 90 weight percent.

25. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 20 to 75 weight percent and said binder is present in an amount of from 25 to 80 weight percent.

26. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 30 to 70 weight percent and said binder is present in an amount of from 30 to 70 weight percent.

27. The process of claim 21 or 23 wherein said drying agent is present in an amount of from 40 to 65 weight percent and said binder is present in an amount of from 35 to 60 weight percent.

28. The process of claim 22 wherein said drying agent comprises an effective amount of a molecular sieve and said binder comprises from 30 to 75 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

29. The process of claim 22 wherein said drying agent comprises 50 weight percent of a molecular sieve and said binder comprises 50 weight percent of a material selected from the group consisting of polyurethane foam and polyisocyanurate foam.

30. The process of claim 22 wherein said binder comprises polyurethane foam.

31. The process of claim 22 wherein said binder comprises polyisocyanurate foam.

32. The process of claim 21 wherein said binder has a laminate structure.

33. The process of claim 23 wherein said superabsorbent polymer comprises sodium polyacrylate or potassium polyacrylate.

34. The process of claim 23 wherein said binder comprises a polyurethane foam.

35. The process of claim 23 wherein said binder comprises a polyisocyanurate foam.

36. The process of claim 23 wherein said binder comprises a support comprising cellulose.

37. The process of claim 36 wherein said support has a laminate structure.

38. The process of claim 20 wherein said halogenated hydrocarbon comprises a hydrofluorocarbon.

39. The process of claim 38 wherein said hydrofluorocarbon comprises difluoromethane.

40. The process of claim 20 wherein said composition further comprises at least one drying agent selected from the group consisting of activated alumina, activated carbon and silica gel.

41. The composition of claim 1 wherein said composition further comprises at least one drying agent selected from the group consisting of activated alumina, activated carbon and silica gel.

42. The process of claim 19 wherein said chemical mixture comprises air.

43. A drier core comprising an effective amount of a composition comprising a drying agent and a binder wherein said drying agent comprises an effective amount of a material selected from the group consisting of superabsorbent polymer, molecular sieve and mixtures thereof and said binder comprises an effective amount of a material selected from the group consisting of polyurethane foam, polyisocyanurate foam and a support comprising cellulose.

44. The drier core of claim 43 wherein said drying agent is present in an amount of from 10 to 80 weight percent and said binder is present in an amount of from 20 to 90 weight percent.

45. The drier core of claim 43 wherein said drying agent comprises superabsorbent polymer.

46. The drier core of claim 43 wherein said superabsorbent polymer comprises sodium polyacrylate or potassium polyacrylate.

47. The drier core of claim 43 wherein said drying agent comprises molecular sieve.

48. The drier core of claim 43 wherein said drying agent comprises a mixture of superabsorbent polymer and molecular sieve.

49. The drier core of claim 44, 45, 46, 47 or 48 wherein said binder comprises polyurethane foam.

50. The drier core of claim 44, 45, 46, 47 or 48 wherein said binder comprises polyisocyanurate foam.

51. The drier core of claim 44, 45, 46, 47 or 48 wherein said binder comprises a support comprising cellulose.

52. The drier core of claim 43 wherein the drying agent further at least one drying agent selected from the group consisting of activated alumina, activated carbon and silica gel.

53. A process comprising the steps of cycling a refrigerant in a system wherein the refrigerant is condensed and thereafter evaporated, the system having therein a drying effective amount of the composition of claim 1.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 June 2000 (22.06.2000)

PCT

(10) International Publication Number
WO 00/35562 A3

(51) International Patent Classification[7]: B01D 53/28, 53/26, F25B 43/00

(21) International Application Number: PCT/US99/30064

(22) International Filing Date: 16 December 1999 (16.12.1999)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/112,546 16 December 1998 (16.12.1998) US
09/291,339 14 April 1999 (14.04.1999) US

(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(72) Inventors: THOMAS, Raymond, Hilton, Percival; 5990 Hopi Court, Pendleton, NY 14094 (US). ROBINSON, Roy, Philip; 38 Andrews Avenue, Cheektowaga, NY 14225 (US). WILLIAMS, David, John; 6202 Shamrock Lane, East Amherst, NY 14051 (US). LOGSDON, Peter, Brian; 38 East Royal Hill Drive, Orchard Park, NY 14127 (US).

(74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc., Law Dept., Attn: A. Olinger, 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

(88) Date of publication of the international search report: 7 September 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/35562 A3

(54) Title: COMPOSITION AND PROCESS FOR SEPARATING WATER FROM CHEMICAL MIXTURES

(57) Abstract: The present invention relates to novel compositions of drying agents of superabsorbent polymers, molecular sieves and mixtures thereof and binders of polyurethane foam, polyisocyanurate foam and supports comprising cellulose and a method for separating, drying and/or filtering chemical mixtures. The composition and method of the invention have broad applicability. They may be used for example to remove water from chemical mixtures like refrigerants (e.g., in vehicular refrigeration systems), air (e.g., in vehicular braking systems), natural gas and cleaning solvents (e.g., used in semiconductor manufacture and pipeline cleaning).

INTERNATIONAL SEARCH REPORT

Intern: ıal Application No
PCT/US 99/30064

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/28 B01D53/26 F25B43/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D F25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 685 897 A (W.A. BELDING ET AL.) 11 November 1997 (1997-11-11)	1,2,5-8, 11,19, 42-44, 47,51
A	claims	4,21, 24-27
Y		20,53

A	EP 0 359 615 A (JAMES RIVER CORPORATION OF VIRGINIA) 21 March 1990 (1990-03-21) cited in the application claims	1,4

	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 April 2000	29. 09. 00

N · dress of the ISA	·. horized ··
·ean Patent Office, P.B. ! NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	BOGAERTS, M

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 594 431 A (MATSUSHITA REFRIGERATION COMPANY) 27 April 1994 (1994-04-27) column 2, line 32 - line 42; claims column 1, line 19 - line 43 ---	1,2,4-8, 11, 14-21, 23-27, 32,33, 36-48, 51-53
A	US 4 013 566 A (R.D. TAYLOR) 22 March 1977 (1977-03-22)	1,2,4-8, 11, 14-19, 21, 23-27, 32,33, 36-48, 51,52
Y	column 1, line 5 - line 51 -----	20,53

1

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [X] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

see annexed sheet

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/

1. Claims: 1(part), 2,4(part),5-8,11,14-18(part),19(part),20(part),21, 23-27(part),32,33(part),36-42,43-46(part),47(part),48(part), 51(part),52(part),53(part)

   Composition comprising a molecular sieve(or a combination of a molecular sieve + a superadsorbent) as drying agent and cellulose as binder; process for using such a composition for removing water from a chemical mixture; drier core comprising such a composition; process for cycling a refrigerant in a system having therein an amount of such a composition.

2. Claims: 1(part),3,4(part),9,10,12,13,14-20(part),22,23-27(part),28-31, 33(part),34,35,43-46(part),49.53(part)

   Composition comprising a molecular sieve (or a combination of a a molecular sieve + a superadsorbent) as drying agent and polyurethane foam or polyisocyanurate foam as binder; process for using such a composition for removing water from a chemical mixture; drier core comprising such a composition; process for cycling a refrigerant in a system having therein an amount of such a composition.

3. Claims: 43-52(part)

   Composition comprising a superadsorbent as drying agent and an effective amount of a binder selected from cellulose, polyurethane foam and polysocyanurate foam.

Information on patent family members

Intern :al Application No
PCT/US 99/30064

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5685897	A	11-11-1997	US	5650221	A	22-07-1997
EP 359615	A	21-03-1990	FI	894094	A	02-03-1990
			NO	893501	A	02-03-1990
			TR	23874	A	16-10-1990
EP 594431	A	27-04-1994	JP	6137720	A	20-05-1994
			JP	3027486	B	04-04-2000
			JP	6235569	A	23-08-1994
			JP	6235570	A	23-08-1994
			DE	69316149	D	12-02-1998
			DE	69316149	T	16-04-1998
			KR	119960	B	22-10-1997
			KR	151546	B	02-11-1998
			US	5402655	A	04-04-1995
			US	5562427	A	08-10-1996
US 4013566	A	22-03-1977	NONE			